DEVELOPMENT OF A METHOD FOR THE DETERMINATION OF IODINE IN SPACECRAFT POTABLE WATER

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FINAL REPORT

ON

Contract NAS9-11861

Prepared by

George P. Whittle
Principal Investigator

OFFICE OF PRIME RESPONSIBILITY,

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Submitted to

The National Aeronautics and Space Administration
Manned Spacecraft Center
Houston, Texas 77058

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University of Alabama
College of Engineering
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BER Report No. 147-14

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ABSTRACT

A one-reagent indicator solution has been prepared for the analysis of iodine concentrations in the range of 0.5 to 12 mg/l of I_2 for use on the potable water proposed for the Skylab project. The indicator solution was formulated to contain the minimum concentrations of reagents for optimum analytical performance. Performance tests indicated that the reagent is stable for at least six months and is reliable for the determination of I_2 under a variety of conditions of I^- concentrations and sample temperatures. Visual estimations as low as 0.5 mg/l were obtained without difficulty and the stability of the developed color allows visual determinations from 0.5 to 12 mg/l of I_2 with a relatively small error.

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SECTION I

INTRODUCTION

1.1 Justification For Study

For extended space flight anticipated in the Skylab project, it is essential that the crew have available a method of determining iodine in the concentration range of 0.5 to 12 mg/l of I_2 in order that the potable water be maintained in a safe microbial condition at all times. The method must be: (1) sensitive, accurate and reproducible; (2) insensitive to constituents other than iodine; (3) easily manipulated and performed; and (4) composed of stable reagents which possess a low toxicity and are non-corrosive to container materials.

1.2 Background

Two methods for iodine determination have been considered for possible use in Skylab. Both of these depend upon the development of a color, visible to the eye, the intensity of which is proportional to the iodine concentration. The iodine concentration in each case is estimated by comparison of the developed color with appropriately colored standards. The two methods are: (1) the starch-cadmium iodide method; and (2) the leuco crystal violet method (LCV). Initial investigations indicated that the starch method is relatively insensitive to iodine concentrations less than 1.5 mg/l and, additionally, the intensity of the developed color is a function of temperature. On the other hand, a preliminary investigation of a modified LCV method indicated that the presence of

iodide ion interferred with color development. While it is thought that the starch method may not be greatly improved because of inherent properties, the same is not true for the LCV method which can be modified in a variety of ways to meet the stated criteria.

1.3 Objective of Study

The specific objective of this study is to modify the leuco crystal violet procedure or otherwise develop a new or modified procedure for determining iodine residuals in spacecraft potable water which will meet the criteria cited in 1.1 above.

SECTION II

TECHNICAL APPROACH

2.1 Theoretical Considerations

On the addition of elemental iodine to water hydrolysis occurs with the formation of hypoiodous acid, HOI, hydrogen ion, and iodide ion.

$$I_2 + H_2O \rightleftharpoons HOI + H^+ + I^- \qquad (1)$$

$$K_h = 3 \times 10^{-13} \text{ at } 25°C$$

In addition, dissociation of HOI takes place with the formation of the hypoiodite ion, OI^-:

$$HOI \rightleftharpoons H^+ + IO^- \qquad (2)$$

$$Ka = 4.5 \times 10^{-13} \text{ at } 25°C$$

At high pH values, conversion of HOI to iodate, IO_3^-, may occur.

$$3HOI + 2OH^- \rightleftharpoons H^+ + IO_3^- + 2I^- + 2H_2O \qquad (3)$$

In distilled water or water with near neutral pH, only Equation (1) is of interest as the concentrations of OI^- and OI_3^- will be insignificant.

In the colorimetric method for iodine proposed by Black and Whittle (1967), the oxidation of leuco crystal violet (LCV) to crystal violet dye was postulated to occur through hypoiodous acid exclusively. The mechanism of this reaction has been described previously (Black and Whittle, 1967 and Whittle, 1969). The oxidation of LCV by I_2 is slow as the production of iodide ion during the course of the reaction opposes the hydrolysis of I_2 and, therefore, the formation of HOI as shown in Equation (1). The addition of mercury as the soluble mercuric chloride results in complexation of iodide ion.

$$HgCl_2 + 4I^- \rightleftharpoons HgI_4^= + 2Cl^- \qquad (4)$$

The stability of the tetraiodide complex is much greater than of any chloro complex.

$$HgI_4^{=} \rightleftharpoons Hg^{2+} + 4I^- \qquad (5)$$

$$K_d = 10^{-31} \text{ at } 25°C$$

$$HgCl_2(s) \rightleftharpoons HgCl_2(aq.) \qquad (6)$$

$$Ks = 2.7 \times 10^{-1} \text{ at } 25°C$$

$$HgCl_4^{=} \rightleftharpoons Hg^{2+} + 4\ Cl^- \qquad (7)$$

$$K_d = 10^{-16} \text{ at } 25°C$$

The reaction in Equation (4) when combined with the hydrolysis in Equation (1) results in the stoichiometric formation of HOI.

$$4I_2 + 4H_2O + HgCl_2 = 4HOI + HgI_4^{=} + 2Cl^- + 4H^+ \qquad (8)$$

The HOI instantaneously oxidizes LCV to the crystal violet dye which in aqueous solution exhibits maximum absorbance at pH 4.0 at 592 nm.

The formation of the very insoluble mercuric iodide,

$$HgI_2 \rightleftharpoons Hg^{2+} + 2I^- \qquad (9)$$

$$Ks = 1.2 \times 10^{-28} \text{ at } 25°C,$$

may be prevented by controlling the mercury-iodide ratio such that complexation is favored over precipitation.

For elemental iodine solutions, Beer's law is followed in the LCV method over a wide range of iodine concentrations with a molar absorptivity of 9×10^4 liter/mole-cm.

2.2 Skylab Considerations

The proposed procedure for disinfection of water aboard Skylab involves treating the water prior to flight to contain near 12 mg/l as I_2. Because of the iodine depletion characteristics during storage, it will be necessary for the flight crew to determine iodine concentrations and, if required, to maintain a certain minimum concentration by injection

of a concentrated stock iodine solution. The limited solubility of elemental iodine in water will require the use of a tri-iodide, I_3^-, solution which has been proposed to contain a 1:2 mole ratio of I_2 to I^- at a total concentration of 30,000 mg/l as I_2. During spaceflight, the I^- concentration will progressively increase not only because of injection of I_3^- but also because of the depletion or reduction of I_2 to I^-. In the LCV procedure, the increasing concentration of I^- in the spacecraft potable water requires an additional consideration of the mercury complexation reaction outlined in previous equations.

The proposed one-reagent container aboard Skylab necessitates redesign of the presently proposed LCV method which now requires two reagents, an indicator and a buffer solution. In addition, the proposed 5:1 sample to reagent ratio proposed for Skylab involves a further modification of the LCV procedure which now employs a 50:1 sample to reagent ratio. The approach to these various modification steps is outlined in the following sub-section.

2.3 Experimental Design

The following are the experimental procedures to be applied for the design and selection of the optimum indicator system.

2.3.1 Reduction of Reagent Concentrations

The proposed sample to reagent ratio of 5 to 1 indicates a 10-fold reduction in reagent concentrations of the presently proposed LCV reagents. Solutions containing reduced concentrations of LCV and $HgCl_2$ will be evaluated for determining I_2 with particular regard to establishing minimum reagent quantities required for the anticipated I_2 and I^- concentrations.

2.3.2 Substitution of New Complexing Agents

Other iodide complexing agents will be evaluated in analytical performance tests in an effort to replace the mercuric chloride salt by a less toxic substance. Mercury salts other than the chloride will also be evaluated for possible reduction of the required mercury concentration.

2.3.3 One Reagent Addition

Efforts to produce a single analytical reagent will be directed toward formulation of: (1) new buffer solutions; (2) combination indicator - buffer systems; and (3) weak acid solutions of the indicator.

2.3.4 Performance Evaluation

All candidate reagent solutions will be evaluated for determining iodine in the concentration range of 0.5 to 12 mg/l of I_2 as a function of increased iodide concentrations. Performance criteria will be: (1) adherence to Beer's law or good reproducibility of results under a variety of conditions; (2) visual estimation of developed colors, particularly the detection of 0.5 mg/l of I_2; (3) minimum complexing agent concentration required for an anticipated I^- concentration; (4) stability of the developed test solution; (5) reproducibility of results for a range of sample temperatures; and (6) stability of the indicator solution (in glass) as a function of storage time.

2.3.5 Selection of Analytical Procedure

The optimum indicator reagent will be selected and recommended for consideration in the Skylab based upon the results of this study.

SECTION III

EXPERIMENTAL

3.1 Reagents

The leuco crystal violet reagent was purchased as Eastman Organic Chemical EK 3651, 4, 4', 4" - methylidynetris(N,N-dimethyaniline). The high quality of this product was such that no additional purification was required.

All acids, salts and other reagents were of reagent grade quality.

The water employed was deionized by a Continental Water Conditioning system to a range of specific resistances of 12 to 18 megohm..

3.2 Equipment

Iodine concentrations were determined employing a Wallace and Tiernan amperometric titrator.

Absorbance values were measured using a Coleman Model 124 Spectrophotometer and a Sargent Model SRG recorder. Absorption cells providing a 10 mm light path length were employed for solutions having absorbance values less than 2.0, and 5 mm cells for solutions having absorbance values greater than 2.0.

3.3 Measurement of Absorbance

The procedure followed for relating absorbance values to iodine concentration involved treating 50 ml of sample with 10 ml of indicator solution. The absorbance of the color developed in the 60 ml total sample was measured using 10 mm cells when the absorbance values were less than 2.0. For absorbance values greater than 2.0, the sample

was initially diluted to 100 ml with dilution water containing the appropriate ratio of sample water to indicator solution. The absorbance of this solution was obtained with 10 mm cells and the initial absorbance in the 60 ml sample was calculated, assuming Beer's law was followed. Later the use of 5 mm cells allowed a direct absorbance reading of the undiluted sample, which was multiplied by two, eliminating any dilution errors.

3.4 Indicator Concentration

For a 50/10 sample to indicator ratio it was calculated than an LCV concentration of 0.25 g per liter would provide a 2.7-fold excess of indicator for stoichiometric recovery of the highest I_2 concentration of 12 mg/l. With the exception of a few trial runs, all indicator solutions were prepared at the concentration of 0.25 g/l of LCV.

A previous study (Black and Whittle, 1967) showed that for indicator solution stability, the pH of the final solution must be 1.6 or less.

3.5 Evaluation of Complexing Agents

For each of the candidate LCV-acid indicators prepared in 3.4 above, the minimum complexing agent required to produce a maximum absorbance value as a function of added I^- concentration was determined as follows, with $HgCl_2$ given as an example.

Prepare the following

$HgCl_2$ solutions:

Solution 1 - 0.250 g/l Solution 2 - 0.625 g/l

Solution 3 - 1.25 g/l Solution 4 - 7.2 g/l

Pipet a 50-ml sample of standardized elemental I_2 solution (0.5 to 12 mg/l) into a 100-ml volumetric flask. Add various combinations of $HgCl_2$ solutions and a strong acetic acid-sodium acetate, pH 4.0, buffer such that the sum of volumes of these solutions equaled 5 ml. To this

was added 5 ml of the indicator solution containing 0.5 g LCV per liter. This procedure was designed to simulate the addition of a mixed indicator composed of LCV, complexing agent, and buffer in the sample/indicator ratio of 5 to 1. For a given I^- concentration, the minimum quantity of $HgCl_2$ required to produce a maximum absorbance value was recorded.

In addition to $HgCl_2$, $Hg(ClO_4)_2$, $Hg(C_2H_3O_2)_2$, $Hg(NO_3)_2$, $HgSO_4$, and other possible complexing agents including Sn(II), Sn(IV), Cu(I), Pt(II), and Pd(II) were evaluated.

New mixed indicator solutions were prepared incorporating the minimum complexing agent required to prevent interference from an assumed maximum concentration of I^- of 70 mg/l. Standard absorbance curves were obtained employing a stock I_3^- solutions prepared on a 1/2 I_2 to I^- mole ratio and containing 30,000 mg/l of I_2.

A stock KI solution was prepared by dissolving 1.300 g of KI in water and diluting to a liter (1 ml = 1 mg I^-). Increments of the KI solution were added to I_3^- solutions to contain various concentrations of I_3^- and added I^- ion. These solutions were then analyzed colorimetrically and the maximum I^- concentration which produced no interference was recorded.

3.6 New Buffer Compositions

In the initial investigations, all samples were treated separately with a strong acetic acid-acetate buffer to produce a sample pH of 4.0, the pH of maximum absorbance of 592 nm. Other buffer compositions were prepared to produce sample pH values of 1.0 to 3.1. The effect of pH on the intensity and hue of the developed color was studied by pH adjustment of solutions of crystal violet dye. Wavelength scans were run to determine the wave length of maximum absorption at each solution pH.

Combination indicator-buffer mixtures were prepared to produce various pH environments in the test sample. Stability tests were initiated to determine the stability toward color development in the indicator-buffer solution and also the ability of the mixed system to reproduce I_2 determinations as a function of the age of the indicator solution.

3.7 One-Reagent Method

Rather than combine the indicator with a buffer solution, solutions of LCV in weak acids were prepared for use as single reagents. Solutions of weak acids have some buffering capacity and if the sample to indicator ratio is near constant, the pH of the final test solution will exhibit a fixed value. Solutions of LCV, compelxing agent, phosphoric acid, and citric acid were prepared and stability test initiated. Standard absorbance curves were prepared as described previously and the maximum I^- interference was recorded.

3.8 Sample to Indicator Ratios

In an effort to improve performance toward iodide interference, the sample to indicator ratios were varied from 50/20 to 50/50 and the results evaluated.

3.9 Temperature Effects

Standardized I_3^- solutions with added I^- concentrations were heated to 35°C and cooled to 5°C and an analysis performed. The performance was evaluated by reference to the standard absorbance curve prepared at room temperature.

3.10 Visual Estimation

The ability to detect as low as 0.5 mg/l of I_2 and the ability to discriminate between adjacent high concentrations of I_2 temporary standards were evaluated by laboratory personnel for the more promising candidate indicator systems.

SECTION IV

RESULTS

4.1 Selection of Complexing Agent

In the investigation where the $HgCl_2$ solution was added separately to the sample prior to the indicator and buffer solutions, the results indicated low $HgCl_2$ concentrations were required for full color development at relatively high added I^- concentrations. This is illustrated in Figure 1 where, for example, only 0.3 g of $HgCl_2$ per liter of mixed indicator solution is required for an I_2 solution containing 25 mg/l of I^-. This study was repeated employing an I_3^- (1:2 I_2 to KI) solution and a mixed indicator solutions containing various concentrations of $HgCl_2$. The results are shown in Table I below.

TABLE I

Minimum $HgCl_2$ Concentration Required for Iodide Ion Concentration. I_2 (as I_3) Concentration Range 0-12 mg/l

Added I^-, mg/l	Total I in 12 mg/l I_2, (1) mg/l	$HgCl_2$, g/l (2)
0	24	0.75
10	34	0.75
20	44	0.75
30	54	0.75
50	74	1.25
70	94	3.60

(1) Based on addition of a 1:2 molar ratio of I_2 to KI.

(2) Based on addition of 5 volumes of sample to 1 volume of mixed indicator 34-1.

This study indicated much higher mercury concentrations are required when a single-step, mixed indicator is employed than when the $HgCl_2$ solution is added separately.

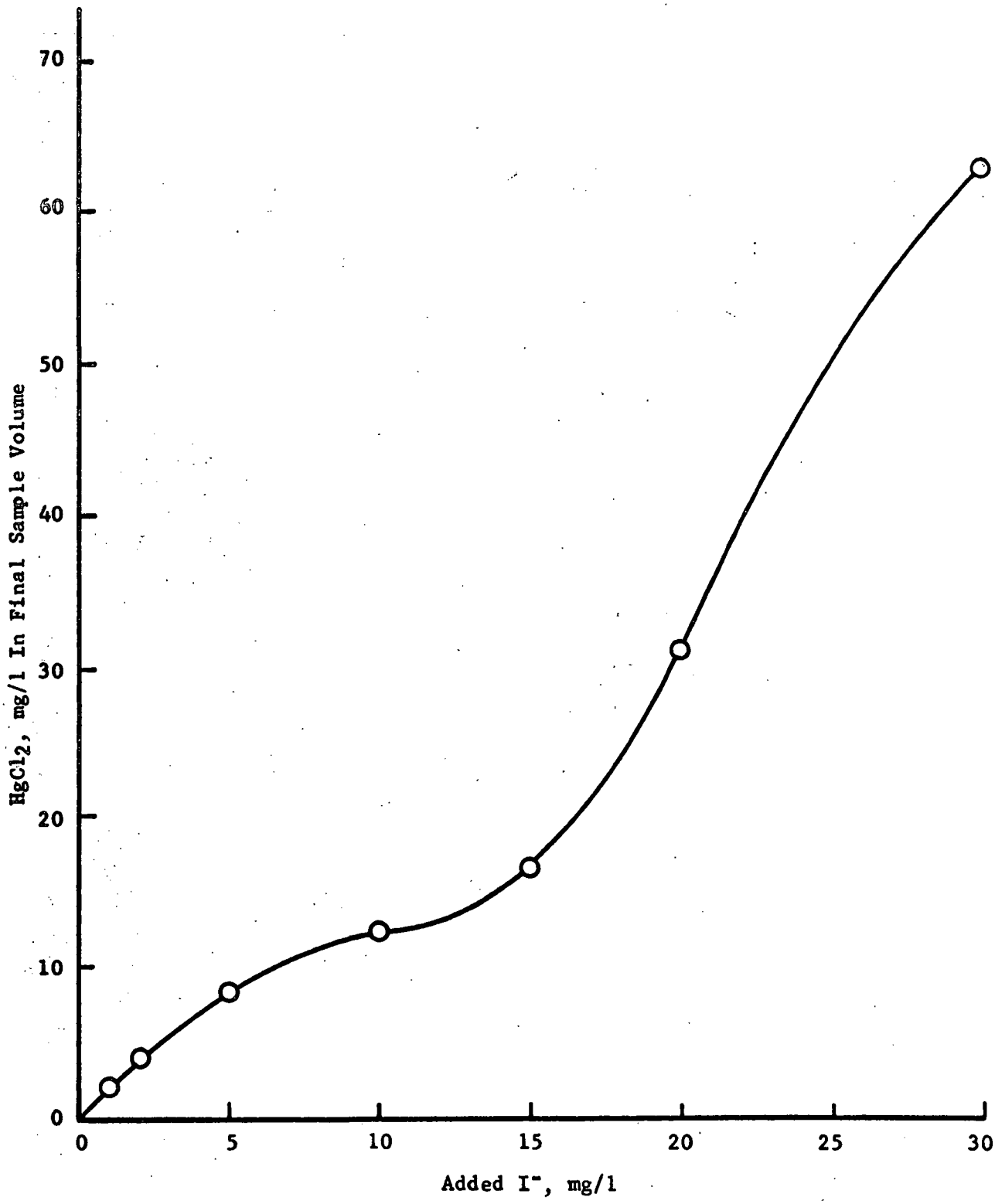

Figure 1. Minimum $HgCl_2$ Concentration to Produce Complete Color Development for Various Iodide Ion Concentrations

Although other mercury salts appeared promising in the initial studies, all exhibited similar relationships with added I^- as shown in Table I. In addition, all mercury salts, with the exception of $HgCl_2$, produced unstable mixed indicator solutions with precipitation being the primary problem.

Palladium salts appeared promising in elemental I_2 solution but precipitation occurred on the addition of I^-, and solutions of these salts produced a dark color on standing.

The results obtained with other complexing agents showed, in most cases, an inability to complex iodide ion and precipitation in mixed indicator solutions.

In Table II below, the results of attempts to formulate mixed indicators are summarized.

TABLE II

Stability of Mixed Indicator-Complexing Agent Systems

Complexing Agent	Stability Results
Mercuric Acetate	Precipitation
Mercuric Nitrate	Precipitation
Mercuric Perchlorate	Precipitation
Mercuric Sulfate	Insolubility
Stannous Chloride	Lack of Complexing Ability
Stannic Chloride	Little Complexing Ability
Platinum Salts	Color Production in Solution
Palladium Salts	Color Production in Solution
Cuprous Chloride	Precipitation
Mercuric Chloride	Stable

In this study, only mercuric chloride exhibited the desired complexing ability and stability in a mixed indicator system and in subsequent studies no other complexing agents were considered further. The concentration of 3.6 g of $HgCl_2$ per liter of indicator solution was adopted as the minimum mercury concentration for an anticipated total I concentration of approximately 94 mg/l.

4.2 Combined Indicator-Buffer Solutions

Several combined indicator-buffer solutions were prepared and evaluated in I_3^- determination tests and for stability as a function of storage time. All solutions contained 3.6 g/l of $HgCl_2$ and initially produced good results for I_3^- concentrations up to 12 mg/l in the presence of 70 mg/l added I^-. Stability tests showed that all solutions with the exception of one exhibited some instability in that a color was formed in the indicator solution with increased storage time. The results of stability tests are summarized in Table III for storage in clear glass bottles. Duplicate storage tests in brown glass bottles showed slightly less color development in all cases. The solution 34-1 was found to be the most stable toward color development. During a total storage time of six months, this solution developed an absorbance of 0.020 which produced a negligible blank correction when added to a sample in the ratio of 5/1 sample to indicator solution.

4.3 Evaluation of One-Reagent Indicators

Because of the superior characteristics of Soln. 34-1, most of the remaining efforts were directed toward determining all characteristics of this indicator in the analysis for iodine. Several other acids were investigated for the solution of LCV and Figure 2 shows a comparison of the absorbance curves obtained with H_3PO_4, H_2SO_4 and HNO_3 as the

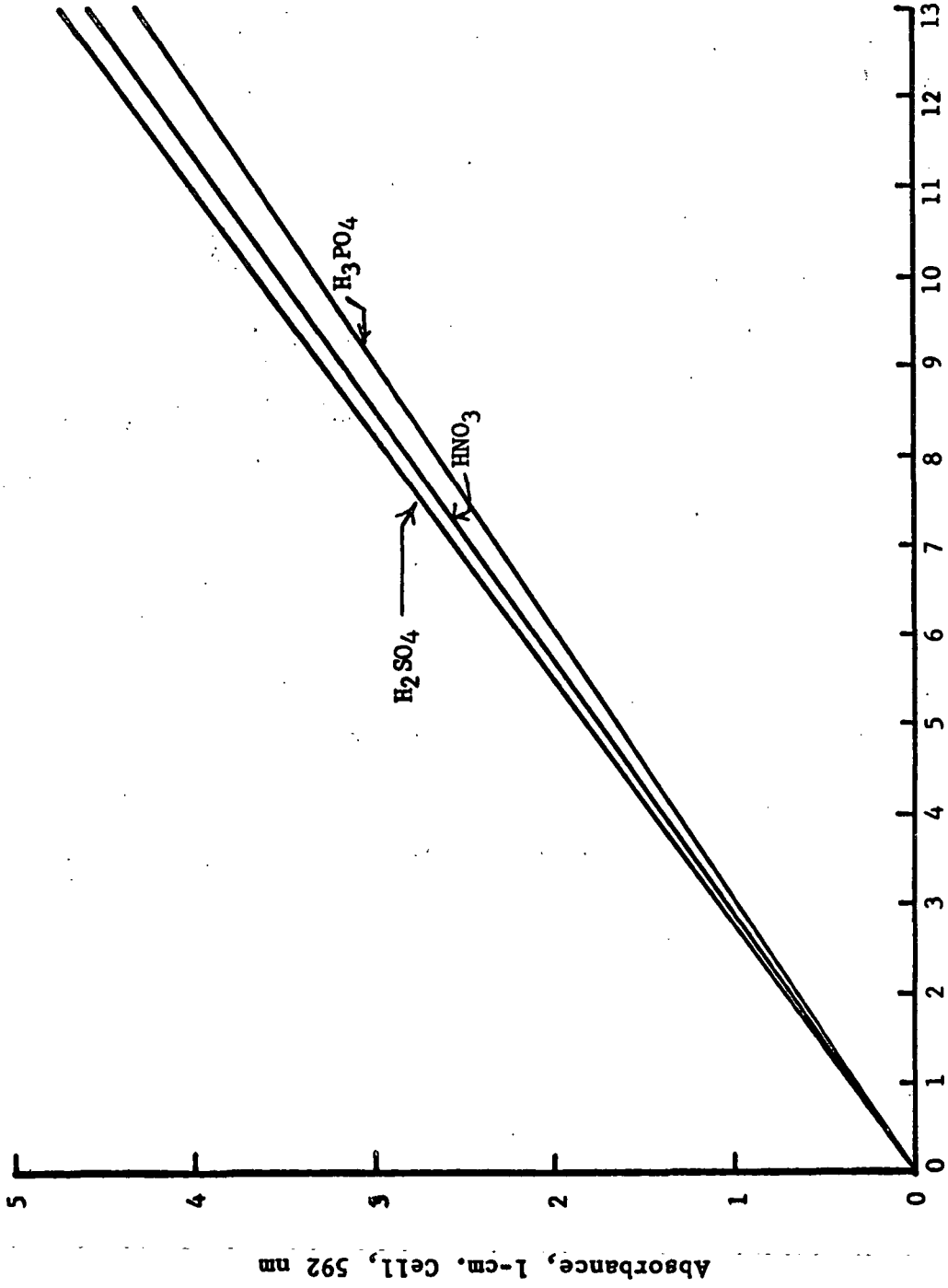

Figure 2. Absorbance Curve for I_2 Concentrations as a Function of the Acid Employed in the Indicator Preparation. Test Run at pH 4.

dissolving acids. In addition, solutions were prepared using perchloric acid. As expected, HNO_3 solutions were unstable toward oxidation of LCV and were not considered further. The H_3SO_4 and $HClO_4$ acid solutions were stable but offered no advantages over the use of phosphoric acid. In addition, these strong acids would have less buffering capacity for slight changes in sample pH than H_3PO_4 and, for these reasons, use of these acids was not considered further.

In an early study, the effect of sample pH on color and absorbance was thought to be simulated by the use of crystal violet dye solutions. It was found, however, that freshly prepared dye solutions adjusted to pH values less than 4.0 did not correspond stoichiometrically to the absorbance values obtained with I_2 solutions at the same sample pH values. In fact, it was observed that on aging the dye solutions increased in absorbance values toward a maximum corresponding to the I_2 stoichiometric value. This inusual and, at the moment, unknown behavior of dye solutions precluded their use in this study. The effect of small changes in sample pH on absorbance values is shown later in this section.

Figure 3 shows the standard absorbance curve obtained with Soln. 34-1 on I_3^- solutions (1:2 I_2 to KI) for the concentration range of 0.5 to 12.0 mg/l. The absorbance values obtained using the initially prepared Solution 34-1, the same solution after 6 months storage, and a recently prepared solution are shown in Figure 3.

The results obtained with fresh and aged Soln. 34-1 in analyses of I_3^- containing added I^- are shown graphically in Figure 4 where the absorbance curve in Figure 3 is used as a reference. The significance of the results shown in Figures 3 and 4 is summarized in the following section, Discussion of Results.

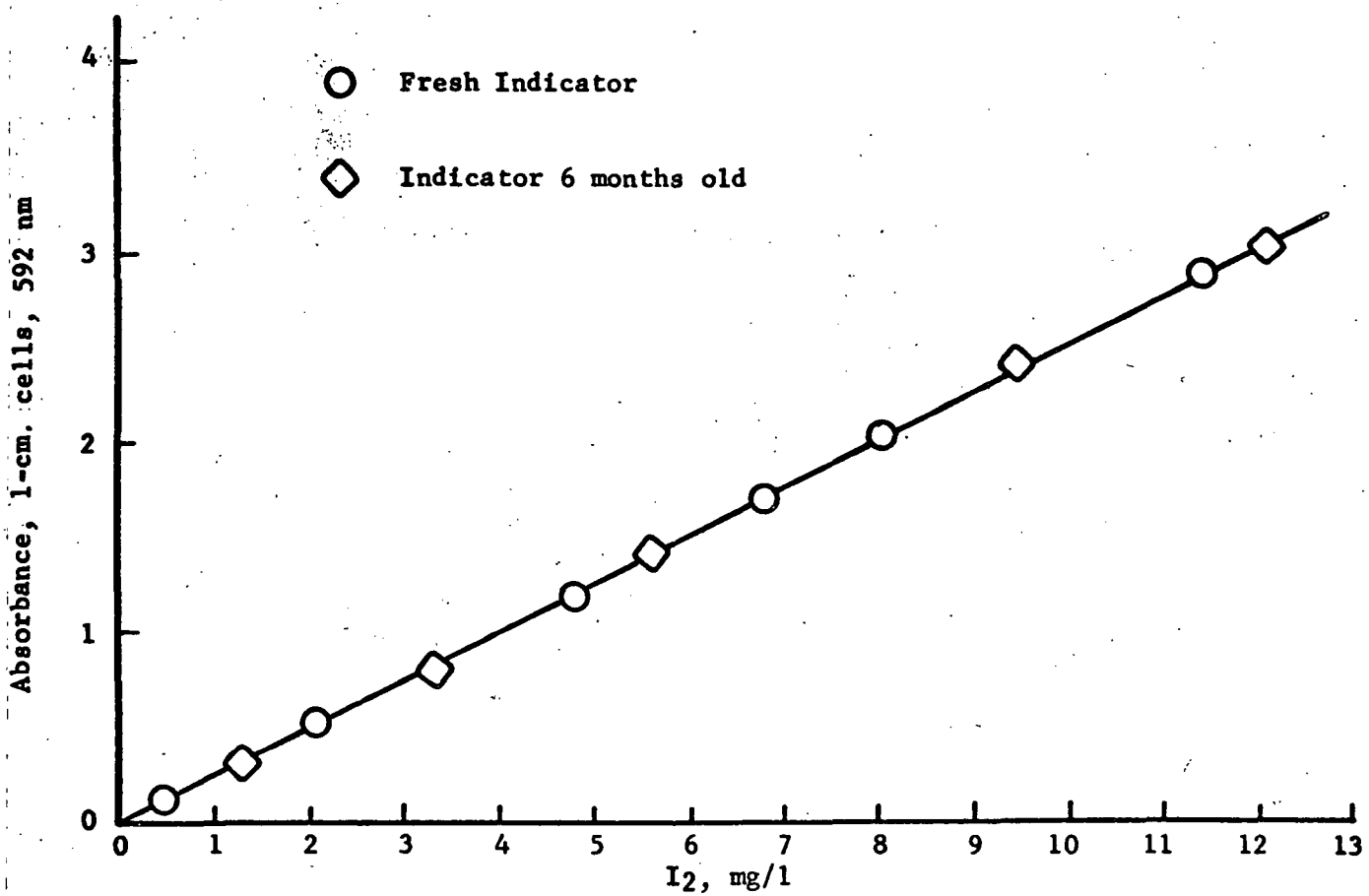

Figure 3. Standard Absorbance Curve Employing Fresh and Six-months Old Solution 34-1.

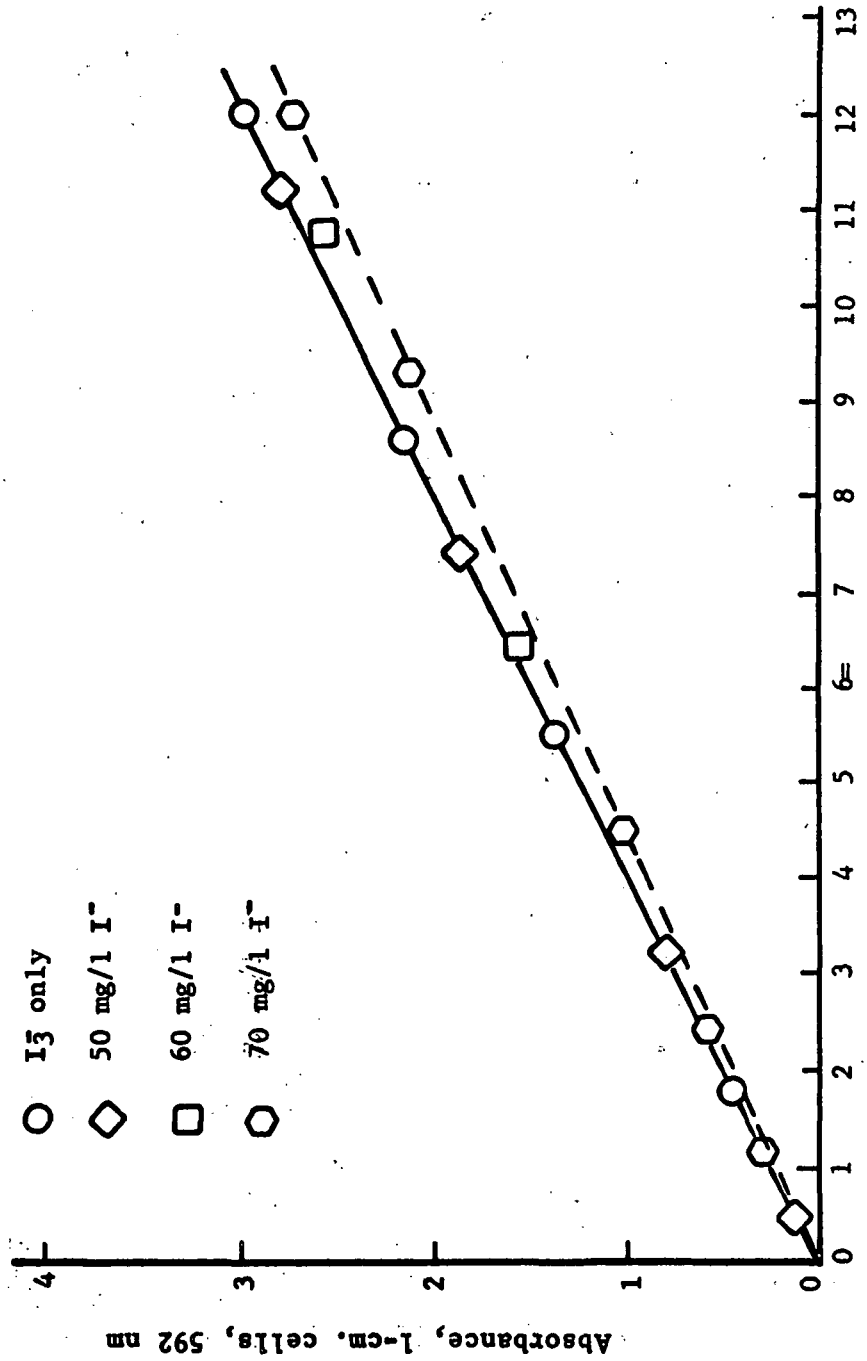

Figure 4. Absorbance Values Obtained as a Function of Added I^- Concentrations Employing Solution 34-1.

The effect of slight changes in sample pH and the sample to indicator ratio is shown in Table IV. Under the heading Percent Relative Error, the errors for changes in sample to indicator ratios are separated from the errors due to changes in sample pH.

4.4 Sample to Indicator Ratios

In an effort to improve the performance of Soln. 34-1, iodine determinations were performed using sample to indicator ratios of 50:20, 50:50, and 50:5. For the low sample to indicator ratios some precipitation of what appeared to be red HgI_2 occurred in solutions containing 70 mg/l of I^-. For the high sample to indicator ratio, lower absorbance values were obtained at high I^- concentrations.

4.5 Temperature Effects

Samples of I_3^- with and without added I^- were heated to 35°C (95°F) and cooled to 5°C (41°F) and analyzed colorimetrically employing Soln. 34-1. The results are shown in Table V.

TABLE V

Effect of Temperature On I_2 Recovery

Titration I_2, mg/l	Added I^-, mg/l	Sample Temp., °C	Colorimetric Abs.	Colorimetric I_2, mg/l	Percent Relative Error
0.8	50	35	0.220	0.7	-1.2
3.2	0	35	0.750	3.1	-3.0
3.4	50	35	0.871	3.5	+3.0
11.2	0	35	2.801	11.2	0.0
11.6	70	35	2,651	10.7	-10.0
0.5	70	5	0.151	0.65	+3.0
2.6	70	5	0.662	2.65	+2.0
10.8	0	5	2.751	11.0	+2.0
10.8	0	5	2.550	10.0	-8.0

4.6 Stability of Developed Colors

The absorbance of developed colors employing Soln. 34-1 were obtained as a function of time. Typical results are presented in the following Table VI.

TABLE IV

Effect of Sample pH and Sample to Indicator Ratio
On I_2 Recovery. Sample Volume, 50 ml.

Indicator Vol. ml	Sample pH	Measured		Volume Corrected		Titration-I_2 mg/l	Percent Relative Error	
		Absorbance	I_2 mg/l	Absorbance	I_2 mg/l		Volume	pH
6	2.5	0.765	3.10	0.69	2.70	2.54	+22.0	+6.3
8	2.4	0.665	2.60	0.643	2.56	2.54	+ 2.4	+0.8
10	2.35	0.636	2.54	-	-	2.54	0	0
12	2.30	0.595	2.40	0.615	2.48	2.54	- 5.5	-2.4
14	2.25	0.590	2.38	0.630	2.50	2.54	- 6.3	-1.6

TABLE VI

Stability of Developed Colors
Soln. 34-1

I_2, mg/l	Added I^-, mg/l	Absorbance-Time in min. 0	5	10	15	60	15 min. Percent Relative Error
2.90	0	0.700	0.695	0.690	0.680	0.630	-3.5
2.90	70	0.690	0.685	0.670	0.660	0.630	-7.0
10.00	0	2.501	2.490	2.45	2.400	2.300	-3.0
10.00	70	2.450	2.420	2.400	2.380	2.350	-6.0

4.7 Visual Tests

A series of temporary I_2 standards were prepared using Soln. 34-1 in the concentration range of 0.5 mg/l to 12.0 mg/l of I_2 in increments of 1 mg/l. These solutions were placed in 15 mm diameter test tubes and mounted on a white background. Iodine solutions were then prepared colorimetrically and presented to several members of the laboratory staff for visual determination.

TABLE VII

Visual Estimation

I_2, mg/l (Unknown)	Added I^-, mg/l	Visual Estimation, I_2, mg/l Person 1	2	3
0.5	0	0.5	0.5	<0.5
0.8	70	0.7	0.6	0.9
1.4	70	1.5	1.5	1.5
2.8	0	3.0	3.0	2.7
4.2	70	4.0	4.0	4.0
6.5	70	6.0	6.0	6.0
9.1	0	9.0	8.5	9.0
10.5	70	9.5	9.2	10.0
11.3	0	12.0	11.0	11.5
11.7	70	10.0	11.0	11.0

SECTION V

DISCUSSION OF RESULTS

5.1 One-Reagent Indicator

The results of this study show that Indicator Solution 34-1 represents the optimum combination of reagents to produce the most stable and reliable one-step indicator. The composition of this solution is repeated below.

Soln. 34-1 (wt./liter)

0.25g LCV
6.9g 85 percent H_3PO_4
3.6g $HgCl_2$

The LCV is first dissolved in about 200 ml of water containing the H_3PO_4. The solution is then diluted to about 900 ml, the $HgCl_2$ added, and after solution is complete, diluted to 1 liter. Best results are obtained when the solution is carried out in a brown glass container.

The use of $HgCl_2$ was required as other mercury salts and other complexing agents failed to produce stable indicator solutions or the desired complexing ability. It is thought that the stability of $HgCl_2$ is due to the fact that the molecule $HgCl_2$ is the predominate species in solution rather than the free mercury ion. Other mercury salts ionize readily to Hg^{2+} which is subject to precipitation as insoluble complexes or salts. The $HgCl_2$ readily exchanges liquids to form the more stable, tetraiodo complex, $HgI_4^{=}$, which allows the reaction between LCV and iodine to proceed to completion.

5.2 Maximum Total I Concentration

The 3.6 g/l of $HgCl_2$ in the indicator solution was originally taken as the minimum amount to allow full color development in high concentrations of I_3^- with added 70 mg/l of I^-. Reference to Figure 5, which shows the results of accumulated data, indicates that up to 50 mg/l of added

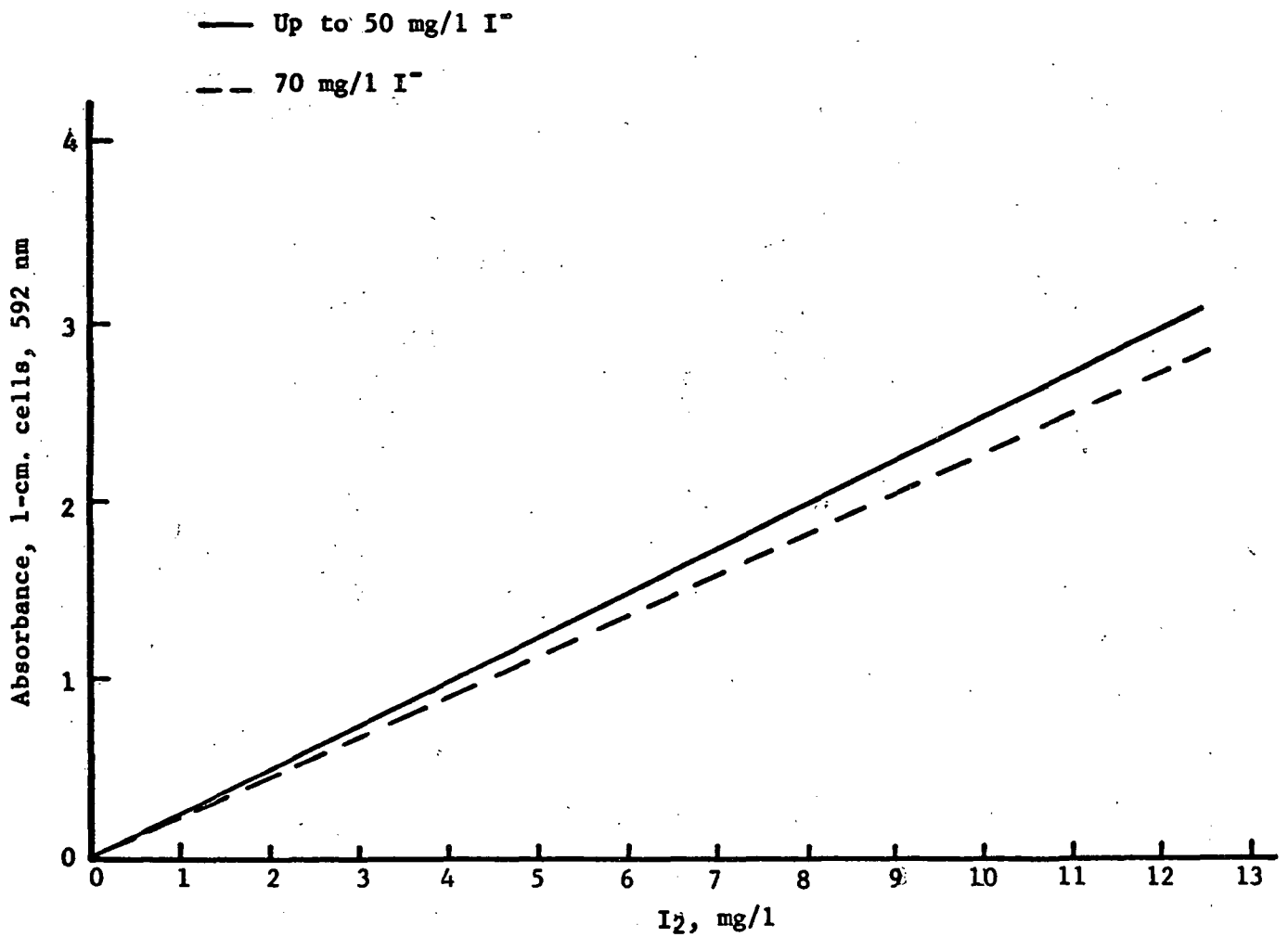

Figure 5. Comparison of Absorbance Values Obtained with Various I^- Concentrations

I^- (74 mg/l total I in a 12.0 mg/l of I_2 as I_3^-) may be safely taken as the upper I^- concentration for full color development. Concentrations of 60 to 70 mg/l of added I^- show somewhat less than full color development. The area between the two curves shown in Figure 5 represents the relative error expected with added I^- of 70 mg/l (94 mg/l total I at 12.0 mg/l I_2 ad I_3^-). The relative error was calculated to be minus 10 percent. The expected errors for selected I_2 concentrations containing 70 mg/l of added I^- are shown in Table VIII.

TABLE VIII

Expected Errors For I_2 Concentrations - 70 mg/l Added I^-

I_2 mg/l	Expected Error, mg/l
0.5	-0.05
3.0	-0.3
6.0	-0.6
10.0	-1.0
12.0	-1.2

In solutions containing added I^- of 50 mg/l or less, the relative error is estimated to be less than $\pm$ 2 percent when the absorbance is measured spectrophotometrically. The visual error is estimated to be about $\pm$ 10 percent relative for I_2 concentrations greater than 10 mg/l. Below 10 mg/l of I_2, visual error is much less and is estimated to be about $\pm$ 5 percent relative.

5.3 Skylab Iodine Addition

The value of 70 mg/l added I^- corresponds to a total I of 94 mg/l when 12 mg/l of I_2 as I_3^- is present. The effort to develop a reliable

test for I_2 under these conditions was based on three dosings of the potable water to 12 mg/l of I_2 during the entire Skylab project, assuming that the I_2 previously dosed had depleted completely to I^-. Under these severe conditions, this would produce in the final mission a concentration of 72 mg/l total I. The goal of 92 mg/l total I would allow one additional dosing to 12 mg/l I_2 or several smaller dosings to maintain the iodine concentration at an acceptable level. The results of this investigation show that the developed LCV test is most reliable up to 74 mg/l total I which corresponds to three maximum dosings to 12 mg/l I_2. Additional dosings to a total of 94 mg/l would produce a relative error of up to -10 percent in the colorimetric test. Since the error is relative, the absolute magnitude of the error would be small in the lower critical I_2 concentrations of 0.5 to 6 mg/l.

5.4 Stability of Reagent

The results indicate that Soln. 34-1 is stable in glass toward color change in the indicator and toward I_2 analysis for a period of at least six months. The final proof of this was the duplication of analytical results using a freshly prepared and a 6 months old reagent.

5.5 Stability of Developed Colors

Some instability of the test color was found by a slight decrease in absorbance with time. No serious error is expected if the color is estimated within 5 minutes with a maximum of -3 to -7 percent relative error for a 15-minute waiting period.

5.6 Effect of Temperature

The results indicate no significant effect of sample temperature on I_2 recovery within the sample temperature range of 35°C (95°F) to 5°C

(41°F). The developed colors produced essentially the same percent relative errors and exhibited the same stability as found with samples analyzed at room temperature.

5.7 Visual Estimation

Visual tests performed by laboratory personnel indicated that as low as 0.5 mg/l of I_2 (or lower) could be easily estimated. From 1.0 to 9.0 mg/l of I_2 the colors were correctly estimated within ± 0.5 mg/l and above 9.0 mg/l most estimations were within ± 1.0 mg/l.

SECTION VI

CONCLUSIONS

A stable, one-reagent indicator solution has been developed which will allow accurate determination of I_2 (as I_3^-) concentrations in the range of 0.5 to 12.0 mg/l. The composition of the solution on a weight per liter of solution basis is given below.

Solution 34-1

0.25g LCV
6.9g 85 percent H_3PO_4
3.6g $HgCl_2$

The presence of iodide ion does not interfere with the test up to 50 mg/l of added I^- or a total of 74 mg/l total I. Above 50 mg/l of added I^-, the relative error is approximately -10 percent. The test has been designed to produce no serious error due to I^- for up to 3 dosings from 0 to 12.0 mg/l of I_2 as I_3^- of the potable water aboard Skylab.

The developed test colors are relatively stable and no significant error will be obtained if the sample is estimated within 5 to 15 minutes after preparation.

Sample temperatures within the range of 35°C (95°F) and 5°C (41°F) produced no significant effect on the developed test.

Visual estimation of as low as 0.5 mg/l I_2 was obtained without difficulty. A visual error of $\pm$ 0.5 mg/l may be expected in the I_2 concentration range of 1.0 to 6.0 mg/l and $\pm$ 1.0 mg/l in the concentration range of 9.0 to 12.0 mg/l.

SECTION VII

RECOMMENDATIONS

It is recommended that the proposed one-reagent indicator, Solution 34-1, be evaluated for stability and performance when stored in Skylab container material for possible use as the analytical reagent for determining iodine during the Skylab project.

REFERENCES

Black, A. P. and Whittle, G. P. New Methods for the Colorimetric Determination of Halogen Residuals: Part I. Iodine, Iodide, and Iodate. Journ. AWWA, 59, (1967).

Black, A. P. and Whittle, G. P. New Methods for the Colorimetric Determination of Halogen Residuals: Part II. Free and Total Chlorine. Journ. AWWA, 59, (1967).

Whittle, G. P. Kinetic Studies of the Reaction of Aqueous Iodine With Organic Matter. Paper presented at the 157th National Meeting of the American Chemical Society, Minneapolis, Minnesota, April 14-18, 1969.

BIBLIOGRAPHY

Sillen, L. G. and Martell, A. E., Stability Constants of Metal-Ion Complexes, The Chemical Society, London, 1964.

Goldstein, Gerald, Equilibrium Distribution of Metal-Ion Complexes, Oak Ridge National Laboratory, ORNL-3620, UC-4-Chemistry, TID-4500 (34th ed.) National Bureau of Standards, Springfield, Virginia.

Butler, J. N. Ionic Equilibrium--A Mathematical Approach, 1964, Addison-Wesley Publishing Company, Reading, Massachusetts.

APPENDIX I

EQUIPMENT PURCHASED WITH CONTRACT FUNDS

1 ea.	S-75631-15 Spectrophotometer, Coleman Model 124	Sargent-Welch Scientific Company Birmingham, Ala.	$3,289.50
1 ea.	S-72180-75 Recorder, Model SRL-G	Sargent-Welch Scientific Company Birmingham, Ala.	1,335.00
1 ea.	S-75643 Long Path Cell Holder	Sargent-Welch Scientific Company Birmingham, Ala.	114.75
1 ea.	S-75646 Cell Holder Temperature Controlled	Sargent-Welch Scientific Company Birmingham, Ala.	263.50
1 ea.	Series A-790 Amperometric Titrator	Wallace & Tiernan, Inc. Belleville, N. J.	360.00
		TOTAL	$5,362.75